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STABILIZED COLOR DEVELOPING COMPOSITIONS AND METHODS OF USING SAME

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STABILIZED COLOR DEVELOPING COMPOSITIONS AND METHODS OF USING SAME

FIELD OF THE INVENTION

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This invention relates to novel color developing compositions that have improved stability because of the incorporation of certain alkyl- or arylsulfonates in combination with organic antioxidants. This invention also relates to methods of using these improved color developing compositions for photoprocessing of color silver halide photographic materials.

BACKGROUND OF THE INVENTION

The basic processes for obtaining useful color images from exposed color photographic silver halide materials include several steps of photochemical processing such as color development, silver bleaching, silver halide fixing, and water washing or dye image stabilizing using appropriate photochemical compositions.

Photographic color developing compositions are used to process color photographic materials such as color photographic films and papers to provide the desired dye images early in the photoprocessing method. Such compositions generally contain color developing agents as reducing agents to react with suitable color forming couplers to form the desired dyes. U.S. Patent 4,892,804 (Vincent et al.) describes conventional color developing compositions that have found considerable commercial success in the photographic industry. Other known color developing compositions are described in U.S. Patent 4,876,174 (Ishikawa et al.), U.S. Patent 5,354,646 (Kobayashi et al.), and U.S. Patent 5,660,974 (Marrese et al.).

It is generally known that the concentrations of various photochemicals used in a photographic color developing composition must be within certain narrow limits in order to provide optimal performance. This is particularly true of "concentrates" or single-part compositions but working

strength compositions formulated from two or more "parts" must also have desired stability of its critical chemical reactants.

A very useful single-part color developing composition that is homogeneous, concentrated, and stable is described and claimed in U.S. Patent 6,077,651 (Darmon et al.). Such compositions are stable from the presence of the free base form of the color developing agent and a particular amount of water-soluble organic solvent.

Stability of the color developing agents in such compositions is generally achieved using sulfite ions or any of the many conventional organic antioxidants (or preservatives) that reduce aerial oxidation rates. For example, U.S. Patent 4,892,804, U.S. Patent 4,876,174, U.S. Patent 5,354,646, and U.S. Patent 5,660,974 (all noted above) describe hundreds of possible derivatives of hydroxylamines that can be used as antioxidants in color developing compositions.

Despite the considerable efforts in the industry to provide stable compositions that will last longer in storage or use, there is a desire in the photoprocessing industry to find additional means for stabilizing color developing compositions, whether single-part or multi-part compositions, and particularly those compositions that contain organic antioxidants such as hydroxylamines.

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SUMMARY OF THE INVENTION

This invention provides a color developing composition having a pH greater than 7 and comprising:

- a) at least 0.0005 mol/l of a color developing agent,
- b) at least 0.0005 mol/l of an organic antioxidant for the color developing agent, and
- c) at least 0.0005 mol/l of a stabilizing compound represented by the following Structure (I):

$$[(R_1)(R_2)N]_m$$
-L- $[SO_3^-M^+]_n$

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(I)

wherein R_1 and R_2 are independently hydrogen or a monovalent aliphatic, heterocyclic, or aromatic group, or R_1 and R_2 are taken together with the nitrogen to which they are attached to form a substituted or unsubstituted 5- to 6-membered heterocyclic ring, m is 0 or 1 such that when m is 0, L is an alkyl or aryl group and when m is 1, L is an alkylene or arylene linking group, M^{+} is a suitable cation to provide a salt, and n is 1, 2, or 3.

In some embodiments, the composition of the present invention is a homogeneous, aqueous single-part color developing composition having a pH of from about 8 to about 14 and comprising:

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- a) from about 0.0005 to about 1 mol/l of a color developing agent in free base form,
- b) from about 0.0005 to about 1 mol/l of a hydroxylamine derivative antioxidant for the color developing agent,
 - c) a water-miscible or water-soluble hydroxy-substituted, straight-chain organic solvent that has a molecular weight of from about 45 to about 300,
 - d) a buffering agent that is soluble in the organic solvent, and
 - e) at least 0.0005 mol/l of a stabilizing compound represented by Structure (I) noted above.

This invention also provides a multi-part color developing composition kit comprising:

- (I) a first aqueous solution having a pH of from about 9 to about 13,
- (II) a second aqueous solution having a pH of from about 3 to about 7 and comprising:
 - (a) at least 0.0005 mol/l of a color developing agent,
- (b) at least 0.0005 mol/l of an organic antioxidant for the color developing agent, and
 - (c) at least 0.0001 mol/l of sulfite ions,
 - (III) an optional third aqueous solution having a pH of from about 10 to about 13.5,

wherein one or both of the first or second aqueous solutions further 30 comprises:

(d) at least 0.0005 mol/l of a stabilizing compound represented by Structure (I) noted above.

Moreover, a color developing composition of the present invention has a pH greater than 7 and comprises at least 0.0005 mol/l of a color developing agent, and at least 0.0005 mol/l of a stabilizing compound represented by Structure (I) noted above.

Further, a method for providing a color image in a color photographic silver halide element comprises contacting the element with an aqueous photographic color developing composition having a pH of from about 7 to about 14 and comprising:

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- a) at least 0.0005 mol/l of a color developing agent,
- 10 b) at least 0.0005 mol/l of an organic antioxidant for the color developing agent, and
 - c) at least 0.0005 mol/l of a stabilizing compound represented by Structure (I) noted above.

In additional embodiments, a method of photographic processing comprises the steps of:

- A) color developing an imagewise exposed color photographic silver halide element with a photographic color developing composition having a pH of from about 7 to about 14 and comprising:
 - a) at least 0.0005 mol/l of a color developing agent,
- b) at least 0.0005 mol/l of an organic antioxidant for the color developing agent, and
- c) at least 0.0005 mol/l of a stabilizing compound represented by Structure (I) noted above, and
- B) desilvering the color developed color photographic silver halide element.

The color developing compositions of the present invention are stabilized by the presence of a combination of an organic antioxidant such as a hydroxylamine and a specific stabilizing compound having Structure (I) noted above. These compounds are alkyl- or arylsulfonic acids. In some embodiments, these compounds are alkylamino- or arylaminosulfonates. These advantages may be obtained to varying degrees with the various embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In some embodiments, the color developing composition of this invention can be formulated as an aqueous concentrate, such as a single-part concentrate, that can then be diluted at least two times with water or buffer (preferably at least four times) to form a working strength color developing composition. Alternatively, a working strength composition of this invention can be prepared by mixing all of the desired components in any desired order at working strength concentrations. Still other embodiments of this invention include two or more parts (usually two or three parts) in a color developing composition kit. Each or all parts can be in concentrated form or provided at working strength concentrations and mixed in the desired proportions to form a working strength solution. Alternatively, one or more concentrated parts can be supplied to a processing vessel as a replenishing solution.

The compositions of this invention contain one or more color developing agents that may be in the form of a sulfate salt or in free base form as a first essential component. Such color developing agents include, but are not limited to, aminophenols, *p*-phenylenediamines (especially N,N-dialkyl-*p*-phenylenediamines) and others which are well known in the art, such as EP 0 434 097A1 (published June 26, 1991) and EP 0 530 921A1 (published March 10, 1993). It may be useful for the color developing agents to have one or more water-solubilizing groups as are known in the art. Further details of such materials are provided in *Research Disclosure*, publication 38957, pages 592-639 (September 1996).

Preferred color developing agents include N,N-diethyl *p*-phenylenediamine sulfate (KODAK Color Developing Agent CD-2), 4-amino-3-methyl-N-(2-methane sulfonamidoethyl)aniline sulfate, 4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate (KODAK Color Developing Agent CD-4), *p*-hydroxyethylethylaminoaniline sulfate, 4-(N-ethyl-N-2-methanesulfonylaminoethyl)-2-methylphenylenediamine sesquisulfate (KODAK Color Developing Agent CD-3), and 4-(N-ethyl-N-2-methanesulfonylaminoethyl)-2-methylphenylenediamine sesquisulfate. Kodak

Color Developing Agent CD-3 is preferred in the processing of photographic color papers.

In preferred embodiments of single-part concentrated compositions, the color developing agents are used in "free base form" as described in U.S. Patent 6,077,651 (noted above), incorporated herein by reference.

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One or more antioxidants are preferably included in the color developing compositions. Inorganic or organic antioxidants can be used as long as one or more organic antioxidants are present. Many classes of useful antioxidants are known, including but not limited to, sulfites (such as sodium sulfite, potassium sulfite, sodium bisulfite and potassium metabisulfite), hydroxylamine (and derivatives thereof), hydrazines, hydrazides, amino acids, ascorbic acid (and derivatives thereof), hydroxamic acids, aminoketones, monoand polysaccharides, mono- and polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, 1,4-cyclohexanediones, and oximes. Mixtures of compounds from the same or different classes of antioxidants can also be used if desired.

Especially useful organic antioxidants are hydroxylamine or its salts and hydroxylamine derivatives as described for example, in U.S Patent 4,892,804 (noted above), U.S. Patent 4,876,174 (noted above), U.S. Patent 5,354,646 (noted above), U.S. Patent 5,660,974 (noted above), and U.S. Patent 5,646,327 (Burns et al.), the disclosures of which are all incorporated herein by reference with respect to antioxidants. Many of these antioxidants are mono- and dialkylhydroxylamines having one or more substituents on one or both alkyl groups. Particularly useful alkyl substituents include sulfo, carboxy, amino, sulfonamido, carbonamido, hydroxy and other solubilizing substituents. More preferably, the hydroxylamine derivatives comprise one or more sulfo, carboxy, or hydroxy solubilizing groups.

Some preferred hydroxylamine derivatives include N,N-diethylhydroxylamine, N-isopropyl-N-ethylsulfonatohydroxylamine, and N,N-di(2-ethylsulfonato)hydroxylamine. Hydroxylamine sulfate is a preferred hydroxylamine salt.

The noted hydroxylamine derivatives can also be mono- or dialkylhydroxylamines having one or more hydroxy substituents on the one or more alkyl groups. Representative compounds of this type are described for example in U.S. Patent 5,709,982 (Marrese et al.), incorporated herein by reference.

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Many of the noted antioxidants (organic or inorganic) are either commercially available or prepared using starting materials and procedures described in the references noted above in describing hydroxylamines.

Also present in the color developing compositions of this invention are one or more stabilizing compounds represented by the following Structure (I):

$$[(R_1)(R_2)N]_m$$
-L- $[SO_3^-M^+]_n$

(I)

wherein m is 0 or 1, and R₁ and R₂ are independently hydrogen or a substituted or unsubstituted monovalent aliphatic group (such as alkyl, cycloalkyl, and similar groups or combinations thereof that can have one or more heteroatoms connecting them), a substituted or unsubstituted heterocyclic group (5- to 10-membered non-aromatic groups having at least one nitrogen, sulfur, oxygen, or sulfur atom in the ring), or a substituted or unsubstituted aromatic group (including carbocyclic and heterocyclic aromatic groups). Preferably, R₁ and R₂ are independently hydrogen or aliphatic groups such as substituted or unsubstituted alkyl groups having 1 to 8 carbon atoms (including methyl and ethyl groups), or a substituted or unsubstituted phenyl group.

Alternatively, R₁ and R₂ can be taken together with the nitrogen to which they are attached to form a substituted or unsubstituted 5- to 6-membered heterocyclic ring (such as a piperazine, N-morpholino, pyrrolidine, or imidazolidine ring). Preferably, such heterocyclic rings have one or more substituents such as one or more -L-SO₃-M⁺ groups.

When m is 1, L is a substituted or unsubstituted alkylene or arylene linking group having up to 16 carbon atoms. Preferably, the alkylene group has 2 to 12 carbon atoms (more preferably 2 to 4 carbon atoms) and is a substituted or unsubstituted straight-chain or cyclic divalent carbocyclic group (such as methylene, ethylene, iso-propylene, and cyclohexylene). The arylene groups can

be substituted or unsubstituted and have 6 or 10 carbon atoms in the aromatic ring (such as phenylene). L can also be a linking group that comprises a combination of alkylene and arylene groups such as alkylenearylene (such as benzylene), alkylenearylenealkylene, and others readily apparent to one skilled in the art.

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When m is 0, L is a monovalent substituted or unsubstituted alkyl or aryl group. Such alkyl groups can be straight-chain, branched, or cyclic groups having from 1 to 12 carbon atoms (such as methyl, ethyl, *iso*-propyl, *n*-hexyl, cyclohexyl, and benzyl). L can also be a substituted or unsubstituted aryl group having 6 to 10 carbon atoms in the aromatic ring (such as phenyl, 3-methylphenyl, and naphthyl).

Also in Structure I, n is 1, 2, or 3. Preferably, m is 1 and n is 1 or 2. More preferably, n is 1.

M⁺ is any suitable cation such as hydrogen, alkali metal cations, ammonium ion, piperidinium ion, or a pyridinium ion.

Representative stabilizing compounds include aminoethanesulfonic acid, 3-(N-(tris(hydroxymethyl)methyl)-amino)propanesulfonic acid, 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid, aminophenylsulfonic acid, 2-(N-morpholino)ethanesulfonic acid, methanesulfonic acid, piperazine-N,N'-bis(2-ethanesulfonic acid), 1-propanesulfonic acid, 2-hydroxy-3-[[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino], 2-[[tris(hydroxymethyl)methyl]-amino]ethanesulfonic acid, 3-(N-morpholino)-2-hydroxypropanesulfonic acid, 3(N-(tris(hydroxymethyl)methyl)amino)propanesulfonic acid, napthalenesulfonic acid, 2-hydroxyethanesulfonic acid, and salts of any of these acids.

These stabilizing compounds are generally present in the color developing compositions in an amount of from about 0.0005 to about 5 mol/l and preferably at from about 0.005 to about 3 mol/l.

In addition, the molar ratio of said stabilizing compound to the antioxidant (when present) is from about 1:20 to about 20:1 (preferably from about 1:5 to about 5:1). The useful ratio will vary depending upon the antioxidant and stabilizing compounds that are used and a skilled worker could perform routine experimentation to determine the optimal amounts of each compound.

The color developing compositions of this invention can advantageously include one or more sequestering agents for calcium or other metal ions. For example, useful calcium ion sequestering agents include polycarboxylic acids each having a molecular weight of from about 2000 to about 100,000 daltons and a plurality of carboxylic acids along the polymer chain. The molecular weight is preferably from about 2000 to about 10,000 daltons. These compounds include poly(acrylic acid), poly(methacrylic acid), poly(itaconic acid), poly(maleic acid), poly(aspartic acid), copolymers derived from the noted carboxylic acid monomers, and other carboxy-containing polyelectrolytes that would be readily apparent to one skilled in the art. Copolymers containing recurring units that do not have carboxy groups are also useful as long as sufficient recurring units contain carboxy groups. Poly(acrylic acid) and poly(acrylic acid-co-maleic acid), or salts thereof, are preferred. The polymers can also be provided in the form of alkali metal or ammonium salts.

Other useful sequestering agents include non-polymeric aminocarboxylic acids (or salts thereof) or polyphosphonic acids (or salts thereof). "Aminocarboxylic acids" is meant to include aminopolycarboxylic acids, polyaminopolycarboxylic acids, and polyaminocarboxylic acids. By "non-polymeric" is meant that the compounds generally have a molecular weight less than 500 daltons.

Aminocarboxylic acids include the many compounds known in the art that are conventionally used as ferric ion bleaching agent ligands. There are many such compounds known in the art including those described in U.S. Patent 4,546,068 (Kuse), U.S. Patent 4,596,765 (Kurematsu et al.), U.S. Patent 4,892,804 (noted above), U.S. Patent 4,975,357 (Buongiorne et al.), U.S. Patent 5,034,308 (Abe et al.), and *Research Disclosure* publications Item 20405 (April, 1981), Item 18837 (December, 1979), Item 18826 (December, 1979), and Item 13410 (December, 1975).

Examples of such compounds include, but are not limited to, ethylenediaminetetraacetic acid (EDTA), 1,3-propylenediaminetetraacetic acid (PDTA), diethylenetriaminepentaacetic acid (DTPA), cyclohexanediaminetetraacetic acid (CDTA), hydroxyethyl-

ethylenediaminetriacetic acid (HEDTA), ethylenediaminedisuccinic acid (EDDS) as described in U.S. Patent 5,679,501 (Seki et al.) and EP-0 532,001B (Kuse et al.). Other useful disuccinic acid chelating ligands are described in U.S. Patent 5,691,120 (Wilson et al.). Aminomonosuccinic acids (or salts thereof) are chelating ligands having at least one nitrogen atom to which a succinic acid (or salt) group is attached, polyamino monosuccinic acids, ethylenediamine monosuccinic acid (EDMS).

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Other classes of biodegradable aminopolycarboxylic acid or polyaminopolycarboxylic acid chelating ligands that can be used to form biodegradable iron complexes include iminodiacetic acid and its derivatives (or salts thereof), including alkyliminodiacetic acids that have a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms (such as methyl, ethyl, n-propyl, isopropyl, and *t*-butyl) as described in EP-A-0 532,003 (Kuse et al.). Particularly useful alkyliminodiacetic acids are methyliminodiacetic acid (MIDA) and ethyliminodiacetic acid (EIDA).

Still other useful aminocarboxylic acids can be represented by the following Structure II:

HOOC-X-N
$$CH_2 \xrightarrow{p} COOH$$

$$CH_2 \xrightarrow{q} COOH$$

wherein p and q are independently 1, 2 and 3, and preferably each is 1. The linking group X can be H, with no carboxy group attached, or it may be any divalent group that does not bind ferric ion and does not cause the resulting ligand to be water-insoluble. Preferably, X is a substituted or unsubstituted alkylene group, substituted or unsubstituted arylene group, substituted or unsubstituted arylenealkylene group, or substituted or unsubstituted alkylenearylene group.

Still other useful aminocarboxylic acids include but are not limited to, β-alaninediacetic acid (ADA), nitrilotriacetic acid (NTA), glycinesuccinic acid (GSA), 2-pyridylmethyliminodiacetic acid (PMIDA), citric

acid, tartaric acid, 1,3-diamino-2-propanetetraacetic acid (DPTA), diethylenetriaminepentaacetic acid (DTPA), and iminodisuccinic acid, and salts thereof.

Polyphosphonic acid sequestering agents are well known in the art, and are described for example in U.S. Patent 4,596,765 (noted above) and *Research Disclosure* publications Item 13410 (June, 1975), 18837 (December, 1979), and 20405 (April, 1981).

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Particularly useful polyphosphonic acids are the diphosphonic acids (and salts thereof) and polyaminopolyphosphonic acids (and salts thereof) described below. Useful diphosphonic acids include hydroxyalkylidene diphosphonic acids, aminodiphosphonic acids, amino-N,N-dimethylenephosphonic acids, and N-acyl aminodiphosphonic acids.

Particularly useful polyphosphonic acids (and salts thereof) are compound that have at least five phosphonic acid (or salt) groups. A mixture of such compounds can be used if desired. Suitable salts include ammonium and alkali metal ions salts. A particularly useful sequestering agent of this type is diethylene-triaminepentamethylenephosphonic acid or an alkali metal salt thereof (available as DEQUESTTM 2066 from Solutia Co.).

Still another polyphosphonic acid includes hydroxyalkylidene diphosphonic acids (or salts thereof). Mixtures of such compounds can be used if desired. Useful salts include the ammonium and alkali metal ion salts. Representative sequestering agents of this class include, but are not limited to, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxy-*n*-propylidene-1,1-diphosphonic acid, 1-hydroxy-2,2-dimethylpropylidene-1,1-diphosphonic acid and others that would be readily apparent to one skilled in the art (and alkali metal and ammonium salts thereof). The first compound is most preferred and is available as DEQUESTTM 2010, and its tetrasodium salt is available as DEQUESTTM 2016D, both from Solutia Co.

Another useful sequestering agent is

morpholinomethanediphosphonic acid or a salt thereof that is available as

BUDEXTM 5103 from Budenheim (Germany). This and similar

cyclicaminodiphosphonic acids (and salts thereof) are described in U.S. Patent 4,873,180 (Marchesano et al.).

It is also possible to include other metal ion sequestering agents (for example, for iron, copper, and/or manganese ion sequestration) in the color developing composition as long as the other conditions of the invention are met.

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One or more buffering agents are generally present in the color developing compositions of this invention to provide or maintain desired alkaline pH of from about 7 to about 14, and preferably from about 8 to about 14. These buffering agents are preferably soluble in the organic solvent described below and have a pKa of from about 9 to about 13. Such useful buffering agents include, but are not limited to carbonates, borates, tetraborates, glycine salts, triethanolamine, diethanolamine, phosphates and hydroxybenzoates. In addition to buffering agents, pH can also be raised or lowered to a desired value using one or more acids or bases such as a hydroxide.

An optional but preferred component of the single-part color developing compositions of this invention is a photographically inactive, water-miscible or water-soluble, straight-chain organic solvent that is capable of dissolving color developing agents in their free base forms. Such organic solvents can be used singly or in combination, and preferably each has a molecular weight of at least 45, and preferably at least 100, and generally 300 or less and preferably 200 or less. Such preferred solvents generally have from 2 to 10 carbon atoms (preferably from 2 to 6 carbon atoms, and more preferably from 4 to 6 carbon atoms), and can additionally contain at least two nitrogen or oxygen atoms, or at least one of each heteroatom. The organic solvents are substituted with at least one hydroxy functional group, and preferably at least two of such groups. They are straight-chain molecules, not cyclic molecules.

By "photographically inactive" is meant that the organic solvents provide no substantial positive or negative effect upon the color developing function of the concentrate.

Useful organic solvents include, but are not limited to, polyols including glycols (such as ethylene glycol, diethylene glycol and triethylene glycol), polyhydroxyamines (including polyalcoholamines), and alcohols (such

as ethanol). Glycols are preferred with ethylene glycol, diethylene glycol and triethylene glycol being most preferred. The most preferred organic solvent is diethylene glycol.

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below in the examples.

The color developing compositions of this invention can also include one or more of a variety of other addenda that are commonly used in photographic color developing compositions, including alkali metal halides (such as potassium chloride, potassium bromide, sodium bromide and sodium iodide), auxiliary co-developing agents (such as phenidone type compounds particularly for black and white developing compositions), antifoggants, development accelerators, optical brighteners (such as triazinylstilbene compounds), wetting agents, fragrances, stain reducing agents, surfactants, defoaming agents, and water-soluble or water-dispersible color couplers, as would be readily understood by one skilled in the art [see for example, *Research Disclosure* publications noted above]. The amounts of such additives are well known in the art also. Representative color developing compositions of this invention are described

It is preferred that no lithium or magnesium ions are purposely added to the color developing compositions of this invention. Depending upon the concentrations of such ions in water used to make up processing solutions, or carried over from previous processing baths, the total concentration (that is, the sum) of these ions remains preferably very low, that is less than 0.0001 mol/l in the compositions, and preferably a total of less than 0.00001 mol/l.

The following TABLES I-A and II-A list the general and preferred amounts of the some components of the color developing compositions (concentrates and working strength compositions, respectively) of this invention. Useful concentrations of components not listed would be readily apparent to one skilled in the art. The preferred ranges are listed in parentheses (), and all of the ranges are considered to be approximate or "about" in the upper and lower end points. During color development, the actual concentrations can vary depending upon extracted chemicals in the composition, replenishment rates, water losses due to evaporation and carryover from any preceding

processing bath and carryover to the next processing bath. The amounts are total concentrations for the various components that can be present in mixtures.

TABLE I-A (CONCENTRATES)

COMPONENT	CONCENTRATIONS
Color developing agent(s)	0.005 - 1 mol/l
	(0.05 - 0.8 mol/l)
Antioxidant(s)	0.005 - 1 mol/l
	(0.05 - 1 mol/l)
Buffering agent(s)	0.5 - 3 mol/l
	(1.5 - 2.5 mol/l)
Calcium Ion Sequestering	1 - 50 g/l
Agent(s)	(2 - 40 g/l)
Stabilizing Compound(s)	0.005 - 5 mol/l
	(0.05 - 3 mol/l)

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TABLE II-A (WORKING STRENGTH)

COMPONENT	CONCENTRATIONS
Color developing agent(s)	0.0005 - 0.25 mol/l
	(0.005 - 0.2 mol/l)
Antioxidant(s)	0.0005 - 0.25 mol/l
	(0.005 - 0.2 mol/l)
Buffering agent(s)	0.002 - 0.8 mol/l
	(0.01 - 0.5 mol/l)
Calcium Ion Sequestering	1 - 25 g/l
Agent(s)	(1 - 20 g/l)
Stabilizing Compound(s)	0.0005 - 2 mol/l
	(0.005 - 1 mol/l)

The following TABLES III-A, IV-A, and V-A show general and preferred concentrations for multi-part color developing compositions of this invention. The stabilizing compound can be in one or more of the solutions as long as it is present in at least one of the solutions (in an amount of at least 0.0005 mol/l). The third solution is optional so the kit can have two or three parts (solutions).

TABLE III-A: FIRST SOLUTION

COMPONENT	CONCENTRATIONS
Antioxidant(s)	0 - 2 mol/1
	(0.05 - 1.5 mol/l)
Calcium Ion Sequestering	0 - 50 g/l
Agent(s)	(2 - 40 g/l)
Buffer	0.5 - 3 mol/l
	(1.5 - 2.5 mol/l)
Stabilizing Compound	0 - 5 mol/l
	(0 - 3 mol/l)
pН	9 - 14
	(9 - 11)

TABLE IV-A: SECOND SOLUTION

COMPONENT	CONCENTRATIONS
Color developing agent(s)	0.0005 - 1 mol/l
	(0.005 - 0.8 mol/l)
Sulfite ions	0.0001 - 0.5 mol/l
	(0.001 - 0.3 mol/l)
Antioxidant	0 - 2.5 mol/l
	(0.02 - 2 mol/l)
Stabilizing Compound(s)	0 - 5 mol/l
	(0 - 3 mol/l)
pH	1 –4
	(1-3.75)

TABLE V-A: THIRD SOLUTION

COMPONENT	CONCENTRATIONS
Buffer(s)	0.5 - 7.5 mol/l
	(1.5 - 6 mol/l)
Stabilizing Compound(s)	0 - 5 mol/l
	(0 - 3 mol/l)
Antioxidant	0 - 2.5 mol/l
	(0.02 - 2 mol/l)
Calcium Ion Sequestering	0 - 50 g/l
Agent(s)	(2 - 40 g/l)
pН	7 – 14
	(10 - 14)

The color developing compositions of this invention have utility to provide color development in an imagewise exposed color photographic silver halide element comprising a support and one or more silver halide emulsion layers containing an imagewise distribution of developable silver halide emulsion grains. A wide variety of types of photographic elements (both color negative and color reversal films and papers, and color motion picture films and prints) containing various types of emulsions can be processed using the present invention, the types of elements being well known in the art (see *Research Disclosure* publication 38957 noted above). In particular, the invention can be used to process color photographic papers of all types of emulsions including so-called "high chloride" and "low chloride" type emulsions, and so-called tabular grain emulsions as well. The color developing composition can also be particularly useful in processing of color negative films.

For example, the present invention can be used to provide color images in photographic color papers including, but not limited to, the following commercial products: KODAK® SUPRA ENDURA Color Papers (Eastman Kodak Company), KODAK® PORTRA ENDURA Color Papers (Eastman Kodak Company), KODAK® ULTRA ENDURA Color Papers (Eastman Kodak Company), KODAK® EKTACOLOR® Generations Color Papers (Eastman Kodak Company), KODAK® ROYAL® Generations Color Papers (Eastman Kodak

Company), KODAK® Perfect Touch Color Paper, KODAK® PORTRA Black and White Color Paper, KODAK® ULTRA III Color Papers (Eastman Kodak Company), Fujicolor Super Color Papers (Fuji Photo Co., FA5, FA7, FA9, Type D and Type DII), Fujicolor Crystal Archive Color Papers (Fuji Photo Co., Digital 5 Paper Type DP, Professional Paper Type DP, Professional Type CD, Professional Type CDII, Professional Type PD, Professional Type PDII, Professional Type PIII, Professional Type SP, Type One, Professional Paper Type MP, Type D and Type C), Fuji Prolaser (Fuji Photo Co.), KONICA COLOR QA Color Papers (Konica, Type QA6E and QA7, Type AD Amateur Digital, Type CD Professional 10 Digital), Konica Color Paper Professional SP (Konica), Konica Color Paper Professional HC (Konica), Konica Color Paper Professional for Digital Type CD (Konica), Agfa Prestige Color Papers (AGFA, Digital and Prestige II), Agfa Laser II Paper (AGFA), Agfa Professional Portrait (AGFA), Agfa Professional Signum II (AGFA), Mitsubishi Color Paper SA Color Papers (Mitsubishi, Type SA-C, 15 Type SA-PRO-L and Type SA-PRO-H).

KODAK® DURATRANS®, KODAK® DURACLEAR, KODAK® EKTAMAX RA and KODAK® DURAFLEX transparent photographic color positive materials and KODAK® Digital Paper Type 2976 can also be processed using the present invention.

20 Representative commercial color negative films that can be processed using the present invention include, but are not limited to, KODAK ROYAL GOLD® Color Films (especially the 1000 speed color film), KODAK GOLD MAX® Color Films, KODAK ADVANTIX® Color Films, KODAK VERICOLOR® III Color Films, KONICA VX400 Color Film, KONICA Super SR400 Color Film, KONICA CENTURIA Color Negative Films, FUJI SUPERIA and NEXIA Color Films, and LUCKY Color Films. Other elements that could be used in the practice of this invention would be readily apparent to one skilled in the art.

Color development of an imagewise exposed photographic silver halide element is carried out by contacting the element with a color developing composition of this invention under suitable time and temperature conditions, in suitable processing equipment, to produce the desired developed color image.

Additional processing steps can then be carried out using conventional procedures, including but not limited to, one or more color development stop, bleaching, fixing, bleach/fixing, washing (or rinsing), stabilizing and drying steps, in any particular desired order as would be known in the art. Useful processing steps, conditions and materials useful therefor are well known for the various processing protocols including the conventional Process C-41 processing of color negative films, Process RA-4 for processing color papers and Process E-6 for processing color reversal films (see for example, *Research Disclosure* publication 38957 noted above), and any known modified protocols.

The color developing compositions of this invention can also be used in what are known as redox amplification processes, as described for example, in U.S. Patent 5,723,268 (Fyson) and U.S. Patent 5,702,873 (Twist).

Processing according to the present invention can be carried out using conventional deep tanks holding processing solutions. Alternatively, it can be carried out using what is known in the art as "low volume thin tank" processing systems, or LVTT, which have either a rack and tank or automatic tray design. These processors are sometimes included in what are known as "minilabs." Such processing methods and equipment are described, for example, in U.S. Patent 5,436,118 (Carli et al.) and publications noted therein. Some minilab processing machines are commercially available as Noritsu 2211SM Printer/Paper Processor, Noritsu 2102SM Printer/Paper Processor, and Noritsu 2301SM Printer/Paper Processor.

Color development is generally followed by desilvering using separate bleaching and fixing steps, or a combined bleach/fixing step using suitable silver bleaching and fixing agents. Numerous bleaching agents are known in the art, including hydrogen peroxide and other peracid compounds, persulfates, periodates, and ferric ion salts or complexes with polycarboxylic acid chelating ligands. Particularly useful chelating ligands include conventional polyaminopolycarboxylic acids including ethylenediaminetetraacetic acid and others described in *Research Disclosure* publication 38957 noted above, U.S. Patent 5,582,958 (Buchanan et al.) and U.S. Patent 5,753,423 (Buongiorne et al.). Biodegradable chelating ligands are also desirable because the impact on the

environment is reduced. Useful biodegradable chelating ligands include, but are not limited to, iminodiacetic acid or an alkyliminodiacetic acid (such as methyliminodiacetic acid), ethylenediaminedisuccinic acid and similar compounds as described in EP 0 532,003A1 (Ueda et al.), and ethylenediamine monosuccinic acid and similar compounds as described in U.S. Patent 5,691,120 (Wilson et al.). Useful fixing agents are also well known in the art and include various thiosulfates and thiocyanates or mixtures thereof as described for example in U.S. Patent 6,013,424 (Schmittou et al.). These references are incorporated herein by reference.

Rinsing and/or stabilizing steps can be carried out after desilvering if desired using various rinsing or stabilizing compositions that may include one or more anionic or nonionic surfactants. Representative compositions and conditions for this purpose are, for example, described in U.S. Patent 5,534,396 (McGuckin et al.), U.S. Patent 5,578,432 (McGuckin et al.), U.S. Patent 5,645,980 (McGuckin et al.), U.S. Patent 5,667,948 (McGuckin et al.), and U.S. Patent 5,716,765 (McGuckin et al.), all incorporated herein by reference.

The processing time and temperature used for each processing step of the present invention are generally those conventionally used in the art. For example, color development is generally carried out at a temperature of from about 20 to about 60°C. The overall color development time can be up to 40 minutes, and preferably from about 12 to about 450 seconds, and more preferably from about 25 to about 120 seconds for photographic color paper and from about 30 to about 360 seconds for color negative film. Conventional conditions can be used for other processing steps including desilvering and rinsing/stabilizing. For example, desilvering can be carried out for from about 30 to about 600 seconds depending upon the type of material being processed and the other processing conditions. The color developing compositions can be replenished at a rate of from about 6 to about 2000 ml/m² of material being processed.

The color developing compositions of this invention can be used as working strength solutions, or as replenishing solutions. The concentrated compositions of this invention can be diluted at least two times (that is, one volume composition to one volume water or buffer), and preferably at least four

times, and up to eight times, to provide a working strength solution or replenishing solution.

The following examples are provided to illustrate the practice of this invention and not to limit it in any way. Unless otherwise indicated, percentages are by weight.

Example 1: Aeration Study of Color Developing Compositions

EKTACOLOR® Prime RA Developer was used, with (Example 1) and without (Comparison A), the addition of 2-aminoethanesulfonic acid (taurine) to prepare working strength color developing compositions having the components shown below in TABLE I. Comparison B contained no hydroxylamine antioxidant. Each composition was monitored, in replicates, under acceleration oxidation at 325 ml/min at room temperature in an opened glass container. A decrease in volume due to evaporation was compensated for by periodically adding deionized water. Each composition was analyzed periodically for the amount of remaining color developing agent (KODAK Color Developer CD-3) and N,N-diethylhydroxylamine antioxidant. The results of these measurements are shown in TABLES II and III below.

20 TABLE I

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Component		Amount	
	Comparison A	Comparison B	Example 1
Water	800 ml	800 ml	800 ml
VERSA TL sulfo-	0.17 g	0.17 g	0.17 g
nated polystyrene			
Triethanolamine	7.3 g	7.3 g	7.3 g
(85%)			
N,N-diethyl-	5.4 g (0.06 mol/l)	0	5.4 g (0.06
hydroxylamine			mol/l)
Taurine	0	0	2.5 g (0.02
			(mol/l)

Component		Amount	
	Comparison A	Comparison B	Example 1
Phorwite REU	1.1 g	1.1 g	1.1 g
MgSO ₄	0.2 g	0.2 g	0.2 g
LiSO ₄	2.0 g	2.0 g	2.0 g
1-hydroxy-	0.86 g	0.86 g	0.86 g
ethylidene-1,1-			
diphosphonic acid			
KCl	4.0	4.0	4.0
KBr	0.03 g	0.03 g	0.03 g
KODAK Color	6.8 (0.016 mol/l)	6.8 g (0.016 mol/l)	6.8 g (0.016
Developer CD-3			mol/l)
K ₂ CO ₃	25 g	25 g	25 g
Water	To make 1 liter	To make 1 liter	To make 1 liter

The pH of each composition was adjusted to 10.8 with H₂SO₄ or KOH.

TABLE II

Time (hours)	KODAK Color	Developer CD-3 Ren	naining (%)
	Comparison A	Comparison B	Example 1
0	100	100	100
24	94.3	40	95.7
48	75.8	0.7	80.0
72	8.08	0	30.8

TABLE III

Time (hours)	N,N-Diethylhydroxy	lamine Remaining (%)
	Comparison A	Example 1
0	100	100
24	48.5	52.2

This study shows that the composition of this invention (Example 1) containing a combination of taurine and N,N-diethylhydroxylamine antioxidant is more stable to decomposition than the standard composition, with or without the antioxidant (Comparisons A and B). A small increase in pH was also observed with the composition of this invention during the evaluation.

Examples 2-4: Various Amounts of Taurine

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We evaluated the use of various levels of taurine in working strength compositions of this invention that were formulated from conventional EKTACOLOR® Prime RA Developer. The compositions, described below in TABLE IV, were monitored under accelerated oxidation as described in Example 1. The compositions were monitored periodically for the amount of remaining Kodak Color Developer CD-3, N,N-diethylhydroxylamine antioxidant, and changes in pH. The results of these measurements are shown below in TABLES V and VI.

TABLE IV

Component			Am	Amount		
	Comparison A	Comparison B	Comparison C	Example 2	Example 3	Example 4
Water	800 ml	800 ml	800 ml	800 ml	800 ml	800 ml
VERSA TL sulfo-	0.17 g	0.17 g	0.17 g	0.17 g	0.17 g	0.17 g
nated polystyrene						
Triethanolamine	6.47 ml	6.47 ml	6.47 ml	6.47 ml	6.47 ml	6.47 ml
(85%)						
-Z, Z	5.4 g (0.06	0	0	5.5 g (0.06	5.4 g (0.06 mol/l)	5.4 g (0.06 mol/l)
diethylhydroxylmine	mol/l)			([/[om		
Taurine	0	0	93.85 g (0.75	25 g (0.2	62.57 g (0.5 mol/l)	93.85 g (0.75
			mol/l)	mol/l)		mol/1)
Phorwite REU	1.1 g	1.1 g	1.1 g	1.1 g	1.1 g	1.1 g
LiSO ₄	2.0 g	2.0 g	2.0 g	2.0g	2.0 g	2.0 g
MgSO ₄	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g
1-hydroxy-	0.86 g	0.86 g	0.86 g	0.86 g	0.86 g	0.86 g
ethylidene-1,1-						
diphosphonic acid						
KCI	4.0 g	4.0 g	4.0 g	4.0 g	4.0 g	4.0 g

Component			Am	Amount		
	Comparison A	Comparison B	Comparison B Comparison C Example 2	Example 2	Example 3	Example 4
KBr	0.03 g	0.03 g	0.03 g	0.03 g	$0.03~\mathrm{g}$	0.03 g
KODAK Color	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016 6.8 g (0.016 mol/l)	6.8 g (0.016 mol/l)
Developer CD-3	mol/l)	mol/1)	mol/l)	mol/l)		
K ₂ CO ₃	25 g	25 g	25 g	25 g	25 g	25 g
Water to make	1 liter	1 liter	1 liter	1 liter	1 liter	1 liter

Each composition was adjusted to pH 10.8 with $\mathrm{H}_2\mathrm{SO}_4$ or KOH.

TABLE V

Time (hours)		KODA	KODAK Color Developer CD-3 Remaining (%)	r CD-3 Remai	ning (%)	
	Comparison A	Comparison B	Comparison B Comparison C Example 2	Example 2	Example 3	Example 4
0	100	100	100	100	100	100
24	96.5	43.6	0.69	99.3	96.2	100
48	86.5	4.21	45.1	88.7	86.0	95.5
72	34.5	0	26.3	54.4	63.0	85.5
			_			

TABLE VI

Time (hours)	N,N-1	Diethylhydroxyl	amine Remaining	g (%)
	Comparison A	Example 2	Example 3	Example 4
0	100	100	100	100
: 48	10.3	13.6	28.0	36.0

These results show that the Comparison C composition containing taurine as the only preservative is more stable than the Comparison B composition containing no preservative and less stable than the standard EKTACOLOR®

Prime RA Developer (Comparison A). The results also show that Examples 2, 3, and 4 containing combinations of taurine are more stable than Comparison A. The combinations of taurine and organic antioxidant appear to synergistically improve the stability of color developing compositions in this environment. Additionally, TABLE VI shows that taurine also improved the stability of the hydroxylamine antioxidant in the compositions. Very little change in pH was observed in all compositions containing taurine.

15 Examples 5-6: Concentrated Single-Part Color Developing Compositions

We also evaluated the use of taurine added to conventional single-part concentrated EKTACOLOR® Prime SP Color Paper Developer that contains much less N,N-diethylhydroxylamine antioxidant. The single-part compositions having the components shown in TABLE VII below were monitored under accelerated oxidation as described in Example 1. The compositions were also monitored periodically for the amount of remaining Kodak Color Developer CD-3 and changes in pH. The results of these measurements are shown below in TABLE VIII.

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TABLE VII

Component		Amount	
	Comparison D	Example G	Example H
Water	12.53 g	12.53 g	12.53 g
Sodium Hydroxide (50%)	3.99 g	3.99 g	3.99 g
N,N-diethylhydroxylamine	4.05 g (0.045	4.05 g (0.045	4.05 g (0.045
	mol/l)	mol/l)	mol/l)
Taurine	0	25.0 g (0.2	62.57 g (0.5
		mol/l)	mol/l)
KODAK Color Developer	6.8 g (0.0156	6.8 g (0.0156	6.8 g (0.0156
CD-3	mol/l)	mol/l)	mol/l)
Diethylene glycol	79.3 g	79.3 g	79.3 g
1-hydroxy-ethylidene-1,1-	0.07 g	0.07 g	0.07 g
diphosphonic acid			
Potassium Carbonate (47%)	45.93 g	45.93 g	45.93 g
Potassium Bicarbonate	1.9 g	1.9 g	1.9 g
KBr	0.025 g	0.025 g	0.025 g
Blankophor REU	1.1 g	1.1 g	1.1 g
Triethanolamine (85%)	2.99 g	2.99 g	2.99 g
DEQUEST® 2066 solution	5.2 g	5.2 g	5.2 g
Water	To make 1 liter	To make 1 liter	To make 1 liter

Each composition was adjusted to pH 10.48 with H_2SO_4 or KOH.

5 TABLE VIII

Time (hours)	KODAK Cole	or Developer CD-3 R	emaining (%)
	Comparison D	Example 5	Example 6
0	100	100	100
24	62.5	66.1	67.3
48	18.4	23.3	33.0
72	3.13	5.41	10.7

These results show that in when taurine is added to the conventional single-part EKTACOLOR® Prime SP Color Developer that contains diethylene glycol and a polyphosphonic acid sequestering agent (DEQUEST® 2066), the stability of the color developing compositions were improved even with a lower amount of hydroxylamine antioxidant. A small loss in pH was observed with the compositions containing taurine.

Examples 7-10: Use of Additional Stabilizing Compounds

- In these examples, we compared the effects from the use of four other stabilizing compounds in combination with the organic antioxidant to stabilize composition to the conventional KODAK EKTACOLOR® Prime RA Developer. The compositions, described in TABLE IX below, were aerated at room temperature and monitored periodically for the amount of remaining

 KODAK Color Developer CD-3, N,N-diethylhydroxylamine antioxidant, and
- KODAK Color Developer CD-3, N,N-diethylhydroxylamine antioxidant, and changes in pH. The results of these measurements are shown in the following TABLES X and XI.

TABLE IX

Component	Comparison A	Example 7	Example 8	Example 9	Example 10
Water	800 ml	800 ml	800 ml	800 ml	800 ml
VERSA TL sulfonated polystyrene	0.17 g	0.17 g	0.17 g	0.17 g	0.17 g
Triethanolamine (85%)	6.47 ml	6.47 ml	6.47 ml	6.47 ml	6.47 ml
N,N-diethylhydroxylamine	5.4 g (0.06 mol/l)	. 0	0	0	5.4 g (0.06
					mol/l)
Piperazine-N,N'-bis(2-	0	60.47 g (0.2	0	0	0
ethanesulfonic acid)		mol/l)			
1-Propanesulfonic acid, 2-hydroxy-	0	0	51.86 g (0.2	0	0
3-[[2-hydroxy-1,1-	,		mol/l)		
bis(hydroxymethyl)ethyl]amino]					
2-[[Tris(hydroxymethyl)methyl]-	0	0	0	45.85 g (0.2 mol/l)	0
amino]ethanesulfonic acid					
Methanesulfonic acid	0	0	0	0	19.22 g (0.2
					mol/l)
Phorwite REU	1.1 g	1.1 g	1.1 g	1.1 g	1.1 g
MgSO ₄	0.2 g	0.2 g	0.2 g	0.2 g	0.2 g
LiSO ₄	2.0 g	2.0 g	2.0 g	2.0 g	2.0 g

Component	Comparison A	Example 7	Example 8	Example 9	Example 10
1-Hydroxyethylidene-1,1-diphos-	0.86 g	0.86 g	0.86 g	0.86 g	0.86 g
phonic acid (DEQUEST® 2010)					
KCI	4.0 g	4.0 g	4.0 g	4.0 g	4.0 g
KBr	0.03 g	0.03 g	0.03 g	0.03 g	0.03 g
KODAK Color Developer CD-3	6.8 g (0.016 mol/l)	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016 mol/l)	6.8 g (0.016
		mol/l)	mol/l)		mol/1)
K ₂ CO ₃	25 g	25 g	25 g	25 g	25 g
Water	To make 1 liter	To make 1 liter	To make 1 liter	To make 1 liter	To make 1 liter

Each composition was adjusted to pH 10.8 with H₂SO₄ or KOH.

TABLEX

Time (hours)		KODAK Color Developer CD-3 Remaining (%)	eveloper CD-3 Re	maining (%)	
	Comparison A	Example 7	Example 8	Example 9	Example 10
0	100	100	100	100	100
24	96.3	100	9.66	100	100
72	54.4	78.2	74.1	72.2	94.1
96	13	31.0	27.1	26.0	54.2

TABLE XI

ime (hours)		N,N-Diethylhyo	N,N-Diethylhydryoxlamine Remaining (%)	aining (%)		
	Comparison A	Example 7	Example 8	Example 9	Example 10	
	100	100	100	100	100	
	52.5	58.7	59.3	55.4	93.7	
-	19.7	25.4	28.8	26.2	77.3	l

TABLE X shows that combinations of hydroxylamine and other sulfonic acid stabilizing compounds synergistically improved the stability of color developing compositions of this invention compared to the conventional

5 EKTACOLOR® Prime RA Developer. Additionally, improved stability of the hydroxylamine and pH were observed.

Example 11: Alternative Stabilizing Compound

We monitored the effects of the use of methanesulfonic acid as a stabilizing compound in combination with N,N-diethylhydroxylamine in a conventional KODAK EKTACOLOR® Prime RA Developer. The compositions shown below in TABLE XII were aerated at room temperature and monitored periodically for the amount of remaining KODAK Color Developer CD-3, N,N-diethylhydroxylamine antioxidant, and changes in pH. The results of these measurements are show in TABLE XIII below.

TABLE XII

Comparison A	Comparison E	Comparison F	Example 11
800 ml	800 ml	800 ml	800 ml
0.17 g	0.17 g	0.17 g	0.17 g
7.3 g	7.3 g	7.3 g	7.3 g
5.4 g (0.06	0 .	0	5.4 g (0.06
mol/l)			mol/l)
0	0	19.22 g (0.2	19.22 g (0.2
		mol/l)	mol/l)
1.1 g	1.1 g	1.1 g	1.1 g
2.0 g	2.0 g	2.0 g	2.0 g
0.2 g	0.2 g	0.2 g	0.2 g
	800 ml 0.17 g 7.3 g 5.4 g (0.06 mol/l) 0 1.1 g 2.0 g	800 ml 800 ml 0.17 g 7.3 g 7.3 g 7.3 g 5.4 g (0.06 mol/l) 0 1.1 g 1.1 g 2.0 g 2.0 g	800 ml 800 ml 800 ml 0.17 g 0.17 g 0.17 g 7.3 g 7.3 g 7.3 g 7.3 g 5.4 g (0.06 mol/l) 0 19.22 g (0.2 mol/l) 1.1 g 1.1 g 2.0 g 2.0 g 2.0 g

Component	Comparison A	Comparison E	Comparison F	Example 11
1-	0.86 g	0.86 g	0.86 g	0.86 g
Hydroxyethylidene				
-1,1-diphosphonic				
acid (DEQUEST®				
2010)				
KCl	4.0 g	4.0 g	4.0 g	4.0 g
KBr	0.03 g	0.03 g	0.03 g	0.03 g
KODAK Color	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016	6.8 g (0.016
Developer CD-3	mol/l)	mol/l)	mol/l)	mol/l)
K ₂ CO ₃	25 g	25 g	25 g	25 g
Water	To make 1 liter	To make 1 liter	To make 1 liter	To make 1
				liter

Each composition was adjusted to pH 10.8 with H₂SO₄ or KOH.

TABLE XIII

Time (hours)	KODA	K Color Develop	er CD-3 Remaini	ing (%)
	Comparison A	Comparison E	Comparison F	Example 11
0	100	100	100	100
24	96.3	47.3	50.7	96.4
48	86.0	7.6	12	87.7
72	36.7	0	0	43.0

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These results show that the use of methanesulfonic acid as a stabilizing agent in combination with the organic antioxidant synergistically improved the stability of the color developing composition. A smaller loss in pH was observed in the compositions containing methanesulfonic acid.

Example 12: Processing of Photographic Color Paper

Samples of conventional KODAK EDGE[®] 8 Color Paper were given a step wedge test object exposure at 1/10 sec with HA-50, NP-11 filters, and 0.3 Inconel on a conventional 1B sensitometer. The samples were then processed with the standard KODAK EKTACOLOR[®] Prime Developer (Comparison A) or the Example 1 composition noted above using conventional EKTACOLOR Process RA-4 conditions and processing chemicals for bleach-fixing and rinsing. After processing, the samples were allowed to dry in the air at ambient temperature. The desired colored images were obtained in all of the samples.

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Example 13: Processing of Color Negative Film

In this example, we evaluated the use of taurine in a color developing composition designed for color negative film processing. The composition also contained both hydroxylamine sulfate (HAS) and N,N-di(2-sulfoethyl)hydroxylamine (BESHA) as antioxidants. The compositions, described in TABLE XIV below, were monitored periodically under accelerated oxidation as described in Example 1 periodically for the amount of remaining KODAK Color Developer CD-4, HAS, BESHA, and changes in pH. The results of these measurements are shown in the following TABLES XV-XVII.

TABLE XIV

Component		Amount	
	Comparison G	Comparison H	Example 13
Water	800 ml	800 ml	800 ml
HAS	2 g (0.12 mol/l)	0	2 g (0.12 mol/l)
BESHA (33.6%)	8.4 g (0.029	0	8.4 g (0.029
	mol/l)		mol/l)
Taurine	0	0	25.15 g (0.2
			mol/l)

Component		Amount	
	Comparison G	Comparison H	Example 13
Diethylenetriamine-	6.4 ml	6.4 ml	6.4 ml
pentaacetic acid,			
pentasodium salt (40%)			
Diethylene glycol	10 ml	10 ml	10 ml
KBr	1.4 g	1.4 g	1.4 g
K ₂ CO ₃	39 g	39 g	39 g
KODAK Color	4.7 g (0.016	4.7g (0.016	4.7g (0.016
Developer CD-4	mol/l)	mol/l)	mol/l)
NaSO ₃	4 g	4 g	4 g
Water	To make 1 liter	To make 1 liter	To make 1 liter

Each composition was adjusted to pH 10.07 with H_2SO_4 or KOH.

TABLE XV

Time (hours)	KODAK Color Developer CD-4 Remaining (%)		
	Comparison G	Comparison H	Example 13
0	100	100	100
24	82.3	52.1	87.5
48	69.8	5.2	77.1
72	50	0	64.6

TABLE XVI

Time (hours)	BESHA Remaining (%)		
	Comparison G	Example 13	
0	100	100	
24	80.2	82.6	
48	57.1	60.9	
72	15.4	23.9	

TABLE XVII

Time (hours)	HAS Remaining (%)		
	Comparison G	Example 13	
0	100	100	
24	74.0	79.0	
48	19.7	27.2	

These results show that the composition of Example 13 containing a combination of taurine and two other hydroxylamine preservatives was more stable to decomposition than the comparison composition containing the hydroxylamines only. A smaller loss in pH was observed in the composition of this invention.

10 Example 14: <u>Processing Color Negative Film</u>

Samples of conventional KODAK ROYAL® Gold 400 Color Negative Film were given a step wedge test object exposure at 1/25 sec. with a DLVA filter and a 3000 K color temperature lamp on a conventional 1B sensitometer. The samples were then processed using the conventional Process C-41 processing conditions and KODAK FLEXICOLOR processing chemicals except that the Example 13 color developing composition was used instead of the conventional color developing composition. After processing, the samples were allowed to dry in the air at ambient temperature. The desired colored images were obtained in all of the samples.

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Example 15: Three-Part Color Developing Kit

A color developing kit of the present invention was prepared in the following manner:

A "first" concentrated aqueous solution was prepared by mixing sodium sulfite (0.055 mol/l), potassium bromide (0.055 mol/l), diethylene glycol (0.45 mol/l), and potassium carbonate buffer (47% solution, 1.4 mol/l). Water

was added to provide 1 liter of concentrated solution. The solution pH was between 11 to 12.

A "second" concentrated aqueous solution was prepared by mixing hydroxylamine sulfate antioxidant (1.2 mol/l), N,N-di(2-sulfoethyl)-

hydroxylamine (0.29 mol/l), diethylenetriaminepentamethylenephosphonic acid, (0.05 mol/l) and taurine (2.0 mol/l). Water was then added to 1 liter of solution. The solution of pH was adjusted to 3.0-3.5 using sulfuric acid.

A "third" concentrated aqueous solution was prepared by mixing sodium metabisulfite (0.2 mol/l) and KODAK Color Developing Agent CD-4 (0.16 mol/l) with water to 1 liter, and the solution pH was adjusted to 2.0-2.5 using sulfuric acid.

These three parts were mixed in a volume ratio of 2:1:1 to prepare a working strength composition of the invention.

15 Example 16: <u>Alternative Three-Part Color Developing Kit</u>

Another three-part kit of this invention was prepared similar to that described in Example 15 except that taurine was placed in Part A. The three solutions were then similarly combined, diluted, and used to prepare a working strength composition of the present invention.

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The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.